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FATIGUE CRACK PROPAGATION IN POLYMERIC MATERIALS.(U)
NOV 78 R W HERTZBERG, J A MANSON DAHC04-74-G-0010
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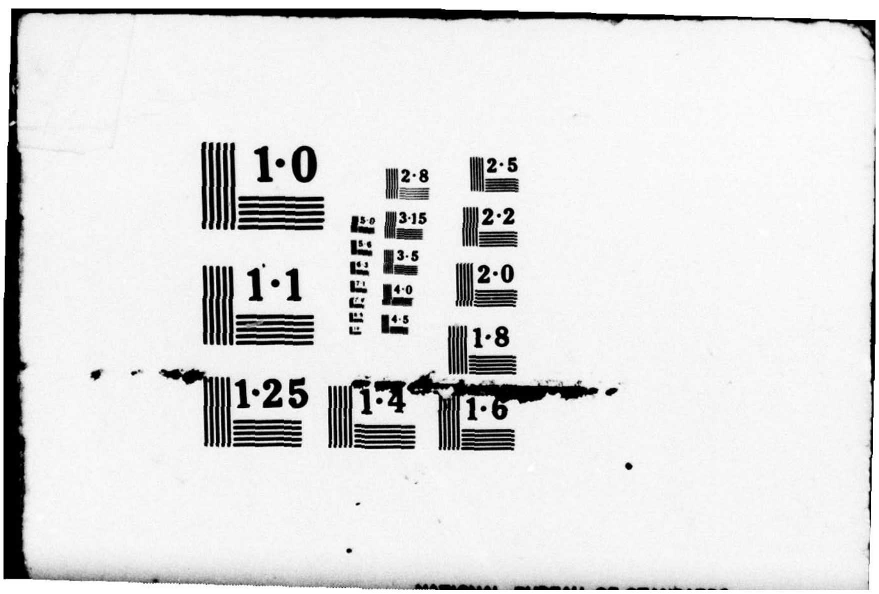
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 19 11180.5-MC, 14409.4-MS	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 Fatigue Crack Propagation in Polymeric Materials		5. TYPE OF REPORT & PERIOD COVERED 9 Final Report. 1 Sep 73 - 24 Sep 78
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 Richard W./Hertzberg, John A./Manson	18 ARO, ARO	8. CONTRACT OR GRANT NUMBER(s) 15 DAHC04-74-G-0010, DAAG29-76-G-0036
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lehigh University, Bethlehem, Pennsylvania 18015		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 13p.
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office, P. O. Box 12211, Research Triangle Park, NC 27709		12. REPORT DATE 11 Nov 78
		13. NUMBER OF PAGES 11
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) LEVEL II		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Plastics	Fatigue Crack Propagation
Fatigue Fracture	Polymeric Materials
Polymer Fatigue	Fracture Mechanics

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes the results of a research program to bring polymer science and fracture mechanics technologies to bear on the subject of polymer fatigue. The first major thrust area concerned an analysis of fatigue fracture micromechanisms in amorphous engineering plastics.

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Final Report

FATIGUE CRACK PROPAGATION IN POLYMERIC MATERIALS

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Grant Nos. DAHC04 74 G0010
DAAG29 76 G0036

Army Research Office-Durham

November 1978

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Army Research Office Grant Numbers

DAHC04-74-G0010 -- 1 Sept. 1973 - 30 August 1976

DAAG29-76-G0036 -- 25 Sept. 1976 - 24 Sept. 1978

Statement of the Problem Studied

The overall objective of the research conducted under ARO-D grant support was to combine a study of fatigue crack propagation (FCP) in polymeric materials using fracture mechanics concepts with a characterization of their molecular, morphological, and both linear and non-linear deformation behavior. To this end, an interdisciplinary research team, involving members from both the Polymer and Mechanical Behavior Laboratories of the Materials Research Center, was assembled to implement the program.

One phase of the research program was designed to study the effect of external test variables such as test frequency, temperature and wave form on fatigue fracture response in numerous polymeric solids. The purpose of this investigation was to determine what effect, if any, hysteretic heating had on the fatigue behavior of engineering plastics. Furthermore, the origin of FCP test frequency sensitivity was to be examined in terms of possible creep-fatigue superposition, strain rate dependence of tensile strength and elastic modulus and/or some type of resonance condition between test machine oscillation rate and molecular main chain or segmental motion jump frequency.

The micro-mechanisms associated with the fatigue fracture process were to be deduced with the aid of transmission and scanning electron microscope observations. Of prime interest was a comparison of fatigue fracture mechanisms observed in various matrix resins under different test conditions. Fatigue striation spacings were to be measured and compared at given ΔK levels with macroscopically determined crack extension rates. Furthermore, the micro-mechanisms associated with discontinuous crack growth were to be examined and a model proposed to explain the genesis of this cracking process. Also, it was necessary to determine the generality of this mechanism in the amorphous polymers other than PVC and in other materials such as rubber-modified and crystalline polymers.

Finally, the FCP response of selected polymeric solids was to be evaluated in terms of internal molecular structure and properties such as molecular weight and molecular weight distribution. Regarding the latter, it was desirable to determine whether FCP sensitivity to M was a function of M_n, M_w or M_z. Other studies were planned to examine the role of second phase additions in enhancing fatigue fracture resistance. Also, changes in FCP rates with internal and external plasticization, cross-linking.

Summary of Major Results

The major intent of this research program was to bring polymer science and fracture mechanics technologies to bear on the subject of polymer fatigue. We feel that this objective was clearly achieved as measured by a number of different criteria. First, the Lehigh blend of interdisciplinary research led to twenty-one joint publications spanning the five years of the grant. Four other papers are presently being drafted, bringing the total number of manuscripts to twenty-five. Second, our successful activities have received the attention of a major book publisher, Academic Press Book Co., who has contracted with us to publish a book dealing with the fatigue behavior of plastics. Third, our research efforts have prompted numerous invitations for us to present papers at both national and international meetings sponsored by the APS, ACS, AIChE, ASTM, SPE, the Plastics and Rubber Institute, and the International Union of Pure and Applied Chemistry in the United States, England, and France. In a related manner, John A. Manson was invited as guest lecturer to the Gordon Conference on Polymers (1978) to discuss ARO-D research findings and Richard W. Hertzberg was invited to deliver the important William Woodside Memorial Lecture at the Detroit Chapter of ASM and spoke on the subject of plastic fatigue.

Considerable progress was made in three principal subject areas and the results of these findings will be discussed separately. First, a major thrust area concerned an analysis of fatigue fracture micromechanisms in amorphous engineering plastics. In certain materials such as polystyrene, polycarbonate, poly(methyl methacrylate) and polysulfone, fatigue striations were found at relatively high stress intensity levels. The spacing between these bands--representing the increment of crack advance resulting from one local excursion--was found to be in excellent agreement with macroscopic crack growth rate measurements and confirmed fracture surface observations to the extent that fatigue striations represented the only operative fatigue fracture micromechanism in this ΔK regime. At lower ΔK levels in these materials as well as in poly(vinyl chloride), ABS and polyacetal, the fracture surface revealed another set of parallel fracture markings. These bands have been identified as discontinuous growth bands whose width corresponds to the dimension of the plastic zone at the advancing crack front as computed from the Dugdale formulation. Video tape images have been used to verify that continuous craze growth occurs during periods where no crack extension is observed. The duration of the successive periods of crack dormancy between sudden bursts of crack extension range from as few as 15 loading cycles to as many as 100,000 cyles, depending upon the material and its structure and the magnitude of the stress intensity factor. It is concluded from this phase of the study that extreme care be exercised when examining the fracture surfaces of plastic components since fatigue fracture lines may represent a single load excursion or as many as 100,000 such load cycles.

A second subject area that received considerable attention during the grant period involved a study of the fatigue crack growth rate dependence on test frequency. Based upon previous polymer fatigue reports available in the open literature, concerning hysteretic heating effects, one would have expected that FCP rates would increase with increasing test frequency. And yet, this was not found to be the case. Instead, numerous polymeric solids exhibited FCP rates which actually decreased with increasing test frequency while other polymers showed no crack growth dependence on test frequency. After considerable experimentation and analysis, it was found that the fatigue crack growth dependence on test frequency was keyed to a resonant condition between the oscillation rate of the test machine and the jump frequency associated with segmental motion corresponding to the β damping peak. Whenever these two frequencies were of the same magnitude, FCP rates were found to decrease with increasing machine oscillation rate. Tests conducted at various temperatures confirmed our prediction that FCP frequency sensitivity could be enhanced or minimized by changing the ambient resonant condition (i.e., temperature) between machine and segmental motion oscillation rates. It has been argued that when resonance does occur, the resulting localized heating at the crack tip provides additional plastic flow that acts to blunt the crack tip, thereby slowing the advance of the crack front.

The third, and perhaps, major focus area has been directed toward an analysis of polymer chemistry and architectural effects on FCP. From our earlier studies, it became clear that the fatigue crack propagation resistance of numerous engineering plastics varied to a much larger degree than that predicted from companion studies of different metal alloy systems. Crystalline structures proved to be superior to amorphous polymers, rubber additions enhanced fatigue resistance, and cross-linking caused crack growth rates to increase. Overall, it was found that the ΔK level required to drive a crack at a specific growth rate increased with increasing material fracture toughness. The effect of internal and external plasticization on crack growth rates was studied in PMMA and PVC, respectively. No significant effect of the external plasticizer, dioctyl phthalate, on FCP rates was found on PVC while additions of butyl acrylate to PMMA produced major changes in fatigue behavior. We concluded from these studies that significant changes in polymeric fatigue response may be expected when basic changes are made to the character of the chains themselves.

The most significant observations with regard to this phase of the grant have dealt with the role of molecular weight and molecular weight distribution on fatigue crack propagation rates and the associated fracture micromechanisms. Though the modulus of elasticity, glass transition temperature and yield strength do not change appreciably with molecular weight above a certain level, fatigue crack growth rates in PVC were found to decrease by at least two orders of magnitude when $\overline{M}$ increased 3½-fold from 66,000 to 225,000. Similarly, a three decade decrease in FCP rates in PMMA accompanied a 50-fold increase in $\overline{M}$. Crack growth rates in these two materials were found to depend on M with a relationship of the form $da/dn \propto e^{1/m} \Delta K^n$. These studies also revealed that the discontinuous crack growth process occurred in polymeric solids only when M was less than about 400,000. Both the fracture mechanism transition and the change in growth rates was related to the relative tendency for craze breakdown based on the concentration of long chain molecules within the craze zone.

Finally, it was confirmed that the presence of a small fraction of high-M or low-M chains exerted a large influence on FCP resistance even when $\overline{M}$ changed little. For example, FCP rates at a constant ΔK level were found to correlate best with the inverse of M_z. As the proportion of low-M ($M \leq M_o$) in high M matrixes were increased, FCP rates at constant ΔK increased in a regular fashion until catastrophic fracture intervened, at about 27 wt% low-M material. When high-M tails were present in low-M matrixes, however, up to ~ 75% low-M material could be tolerated before catastrophic fracture. Thus, it appears that for a given fraction of low M component in a bimodel blend, the fatigue response depends upon the polymerization sequence. These results may be interpreted in terms of the relative ability to form stable entanglement networks.

Grant Publications

The five-year term of this grant was highlighted by considerable progress, resulting in the publication of twenty-one (21) scientific articles in various technical journals and conference proceedings. Four additional manuscripts are currently being drafted and should be submitted for publication by the end of this calendar year. Finally, the principal investigators are in the process of completing a monograph entitled "Fatigue Processes in Engineering Plastics" that is to be published in late-1979 by the Academic Press Book Company. The results from this ARO-D program will serve as a major focus in this treatise.

The list of publications which follows has been divided into three sub-sections to reflect the achievements made in three major research thrust areas described in the previous section. While a number of these papers deal with more than one or all three major subject areas, they are listed in only one sub-section. A fourth section is added to indicate the subject matter of the manuscripts currently being drafted.

John A. Manson Richard W. Hertzberg

<u>Published or in Press</u>

A. Material variables affecting FCP:

1. "Fatigue Crack Propagation in Polycarbonate," J. A. Manson, R. W. Hertzberg, S. L. Kim and W. C. Wu, <u>Coatings and Plastics Preprints</u>, ACS, Div. of Organic Coatings and Plastics Chemistry, Vol. 34(2), p. 268 (1974).

2. "Effect of Molecular Weight on Fatigue Crack Propagation in PMMA," S. L. Kim, M. Skibo, J. A. Manson and R. W. Hertzberg, <u>Polymer Preprints</u>, 16(2), p. 559 (1975).

3. "Effect of Molecular Weight and Plasticization on Fatigue Crack Propagation in PMMA," S. L. Kim, M. Skibo, J. A. Manson and R. W. Hertzberg, <u>Polymer Preprints</u>, <u>17</u>(1), p. 65, 1976.

4. "Effect of Molecular Weight on FCP in PVC," M. Skibo, J. A. Manson, R. W. Hertzberg and E. A. Collins, <u>Proceedings</u> 2nd International Conference on Poly(vinyl chloride), p. 250, 1976.

5. "Fatigue Crack Propagation in Polycarbonate," J. A. Manson, R. W. Hertzberg, S. L. Kim, and W. C. Wu, <u>Toughness and Brittleness of</u> Plastics, Adv. in Chem. Ser., <u>154</u>, p. 146, (1976).

6. "Fatigue Testing," R. W. Hertzberg and J. A. Manson, <u>Plastics</u> World, <u>35</u>(5), p. 50 (1977).

7. "Fatigue Crack Propagation in Poly(methyl methacrylate): Effect of Molecular Weight and Internal Plasticization," S. L. Kim, M. D. Skibo, J. A. Manson and R. W. Hertzberg, <u>Polym. Eng. Sci</u>., <u>17</u>(3), p. 194 (1977).

8. "Fatigue Crack Propagation in Polyacetal," R. W. Hertzberg, M. D. Skibo and J. A. Manson, <u>J. Mater. Sci</u>., <u>13</u>(5), p. 1038 (1978).

9. "Fatigue Crack Propagation Response of Toughened Engineering Plastics," M. D. Skibo, J. Janiszewski, R. W. Hertzberg and J. A. Manson, <u>Proceedings</u>, Symposium on Toughening of Plastics, The Plastics and Rubber Institute, London, England, p. 25.1 (July 1978).

10. "Effect of Molecular Weight Distribution on Fatigue Crack Propagation in Polymers," S. L. Kim, J. Janiszewski, M. D. Skibo, J. A. Manson and R. W. Hertzberg, <u>ACS Organic Coatings and Plastics Chemistry</u>, <u>38</u>(1), p. 317 (1978).

11. "Fatigue Crack Propagation in PVC. 2. Combined Effects of Rubbery Inclusions and Molecular Weight," M. D. Skibo, J. A. Manson, S. M. Webler, R. W. Hertzberg and E. A. Collins, accepted, to ACS Symposium Series, Sept. 1978.

12. "Effect of Molecular Weight Distribution on Fatigue Crack Propagation," S. L. Kim, J. Janiszewski, M. D. Skibo, J. A. Manson and R. W. Hertzberg, in press, Polym. Eng. Sci.

13. "Fatigue Crack Propagation in Rubber-Modified Plastics," M. D. Skibo, J. Janiszewski, S. L. Kim, R. W. Hertzberg and J. A. Manson, Proceedings, 36th Ann. Tech. Conf., Society of Plastics Engineers, p. 304 (1978).

B. Frequency dependence of FCP:

14. "Frequency Sensitivity of Fatigue Processes in Polymeric Solids," R. W. Hertzberg, J. A. Manson and M. Skibo, Journal of Polymer Engineering and Science, 15(4), p. 252 (1975).

15. "The β Transition and Frequency Sensitivity in Fatigue Crack Propagation of Polymers," J. A. Manson, R. W. Hertzberg, S. L. Kim and M. D. Skibo, Polymer, 16, p. 850 (1975).

16. "The Effect of Temperature on the Frequency Sensitivity of Fatigue Crack Propagation in Polymers," M. D. Skibo, R. W. Hertzberg and J. A. Manson, Fracture 1977, 3, ICF4, 1977, p. 1127.

17. "A Correlation Between Fatigue Fracture Properties and Viscoelastic Damping Response in Engineering Plastics," R. W. Hertzberg, J. A. Manson and M. D. Skibo, Polymer, 19(3), p. 358 (1978).

18. Discussion of "A Model of Fatigue Crack Growth in Polymers," R. W. Hertzberg, M. D. Skibo, J. A. Manson and J. K. Donald, submitted to J. Materials Science.

C. Micromechanisms of FCP:

19. "Fatigue Fracture Processes in Polystyrene," M. D. Skibo, R. W. Hertzberg and J. A. Manson, J. Mater. Sci., 11, p. 479 (1976).

20. "On the Generality of Discontinuous Fatigue Crack Growth in Glassy Polymers," M. Skibo, R. W. Hertzberg, J. A. Manson and S. L. Kim, J. Mater. Sci., 12, p. 531 (1977).

21. "Fatigue Fracture Micromechanisms in Engineering Plastics," R. W. Hertzberg, M. D. Skibo and J. A. Manson. Presented at ASTM Symposium on Fatigue Mechanisms, Kansas City, Missouri, May 1978.

Manuscripts in Preparation

22. "Fatigue Fracture Surface Micromorphology in Variable MWD PMMA," J. Janiszewski, R. W. Hertzberg and J. A. Manson.

23. "Effect of Molecular Weight on Fatigue Fracture Frequency Sensitivity in Glassy Polymers," J. Janiszewski, R. W. Hertzberg and J. A. Manson.

24. "Fatigue Crack Growth Behavior and Fracture Micromechanisms in Rubber-Modified Plastics," M. D. Skibo, J. Janiszewski, R. W. Hertzberg and J. A. Manson.

25. "Correlation of Fracture Toughness with Fatigue Crack Propagation in Polymers," S. L. Kim, J. A. Manson, and R. W. Hertzberg.